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Nanomaterials exposure as an occupational risk in metal additive manufacturing

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Abstract. Metal Additive Manufacturing (AM) is a process of joining metallic materials based on 3D model data, aiming the manufacture of three dimensional parts by the successive addition of material, usually layer upon layer. This technology is nowadays seen as an emerging one, showing exceptional perspectives of growth, being able to produce parts in various materials such as precious metals (for example gold, silver and platinum) and several metal alloys, such as aluminium, titanium, nickel, cobalt and magnesium based alloys, among others. However, as the range of feedstock materials, technologies and applications increases, so do the concerns about its impact on health and safety of those who are exposed to the particles emitted during these processes, particularly when AM uses metal powder. Regarding emissions, studies thus far show that nanomaterials are emitted during AM processes, a fact that rises the concern about its impacts and enhances the complexity of risk management on these processes. When risk management aims nanoscale, it becomes a true challenge as it deals with several different nanomaterials and the lack of systematic and standardized risk assessment methodologies. At this scale, risk management raises many doubts regarding the selection of quantitative or qualitative approaches, the identification, characterization and quantification of nanomaterials, the definition of occupational exposure limits and the outlining of control measures. Having this conscience, a review was developed to summarize some of the recent developments in the field of risk management of occupational exposure to nanomaterials during metal additive manufacturing. Additionally, this review emphasizes the need for more investigation about risks regarding nanomaterials in workplaces, which is essential to ensure workers' safety conditions and preserve their health, as well as to make conscious decisions on risk assessment, public health, medical monitoring and control measures, namely the adoption of personal protective equipment.

1. Introduction

Technology evolution made possible the manufacturing of three dimensional parts from 3D model data by using the concept of printing. This process is known by Additive Manufacturing (AM) and consists in joining feedstock materials such as powder, wire or sheets, typically layer upon layer, to create 3D parts by the successive addition of material [1]. Reducing material costs and simplifying processes are two of the many advantages of AM over conventional manufacturing, so this technology is now seen as an emerging one [2].



AM has various applications in different fields, for example, medicine, aerospace industry, energy, jewellery, cosmetic, automotive sector and architecture, having also domestic applications nowadays [3]. There are different AM process categories, such as vat photopolymerization, material jetting, binder jetting, powder bed fusion, material extrusion, direct energy deposition and sheet lamination, as described in the Standard ISO 17296-2:2015, each one of them with particular characteristics. Nevertheless, these processes are permanently being updated and improved, so they cannot be listed exhaustively and strictly. As for materials, AM processes use a large type of materials, including metals, ceramics, polymers and composites [3].

Regarding metal additive manufacturing, significant advances were achieved in the last twenty years, allowing the fabrication of components in complex structural shapes, that are difficult or even impossible to fabricate by subtractive manufacturing methods [1].

The fact that metal 3D printing is a growing technology, capable of using a wide-range of metallic materials, counting nickel, chromium, aluminium and titanium alloys, and different technological processes, poses a challenge in terms of assessing health and safety impacts on workers, which will require tailored approaches [4]. Investigation regarding metal AM impact on health and safety has a large scope, particularly when it comes to its emissions, being necessary to develop studies about toxicology of emitted particles, approaches for exposure assessment, exposure control measures, potential health impacts of exposure to ultrafine particles, among others [4]. A deeper look to ultrafine particle can lead to nanoscale, as this scale designates the length interval approximately from 1 to 100 nanometers (nm) [5]. In accordance with Standard ISO 80004-2:2015, most nanoparticles, defined by their geometrical dimensions, are ultrafine particles when measured.

Studies thus far show that during 3D printing processes nanomaterials are emitted, with diverse emission rates, depending on the experimental design, modelling, temperature applied, and materials used [2]. Judging from studies carried out previously, concerning possible impacts of human exposure to metal nanomaterials, for example during welding, it becomes clear that it is of extreme relevance to study deeply the risk of occupational exposure to nanomaterials during metal 3D printing, including both incidental and engineered nanomaterials.

This paper provides a comprehensive review of literature on occupational risk management of exposure to nanomaterials, when emitted during metal additive manufacturing processes, emphasizing the need of deeper research in this field.

2. Methods

Given their size, surface area and other characteristics (mainly electronic, optical, mechanical and chemical) nanomaterials have exceptional properties, that make them as useful as harmful for the environment and human health [6]. Due to a greater awareness of researchers and regulators regarding environmental, health and safety impact of nanomaterials, the number of studies in this field has been increasing in the last fourteen years, although the majority of them have focused on nanotoxicology [7]. Therefore, more research on risks including the monitoring and characterization of nanomaterials is essential to ensure workers' safety conditions and preserve their health, as well as to make conscious decisions on risk assessment, public health, medical monitoring and use of appropriate personal protective equipment [8]. Thus, the challenges in risk management begins when dealing with the diversity of nanomaterials and the lack of systematic and standardized risk assessment methodologies [7].

To assess the risk of exposure to nanomaterials there are many possible approaches that can be classified into two main groups: qualitative and quantitative methods [9], although some authors begin to propose semi-quantitative approaches as well [10].

2.1. Risk management regarding occupational exposure to nanomaterials – An overview on quantitative approaches

Nanomaterials can be characterized and quantified using different approaches, which allow a quantitative approach to risk management. The quantitative methods commonly used in occupational safety field are based on the measurement of the concentration of particles (or other chemical agents) in the atmosphere, collecting samples of air in the workers' breathing zone, considering the duration of the exposure. Usually, after the sampling and measurement procedures, the level of exposition obtained is compared to the corresponding exposure limit value set for that agent to assess the risk of exposure, considering the concentration and exposure time. However, when it comes to nanoscale, even in assessments that involve well-known nanomaterials, there are many uncertainties when choosing the most appropriate quantitative method [9]. On the other hand, occupational exposure limits (OELs) are not defined for all nanomaterials. For engineered nanomaterials with sufficient data, OELs were defined based on quantitative risk assessment; for others the base point were the qualitative methods, although nowadays quantitative data is available so there is a risk that this OELs are not the most proper; and additionally, there are other nanomaterials, engineered and incidental, with no OEL yet defined [11].

Due to this lack of established and accurate OELs for nanomaterials, as well as to the fact that nanomaterials have distinct characteristics and have often unstable behaviour, it is still a challenge to define which characteristics of nanomaterials and which methods of characterization and quantification are relevant for hazard identification and risk assessment.

If considered that particle size is important for risk assessment, analytical techniques can be useful to characterize nanomaterials. For instance, microscopic techniques are frequently used to characterize nanoparticles, such as: Atomic Force Microscopy (AFM) that provides information on size, morphology, surface texture and roughness; Scanning Tunneling Microscopy (STM) which gives chemical characterization; Scanning and Transmission Electron Microscopy (SEM and TEM) analysing surface, crystal structure, elemental composition, size, shape and other properties; among others [6]. All the same, quantitative approaches can be based on other techniques, for example: light scattering for particle size characterization, such as Dynamic Light Scattering (DLS); X-ray which provides information on surface properties and coatings, crystallographic structure or elemental composition; Spectroscopic for details on size, aggregation, structure, stabilization and surface chemistry; Nanoparticle Tracking Analysis (NTA) that sizes particles from the range of 30 to 1000 nm; or Hyperspectral Imaging that delivers information on spatial distribution and spectral characteristics [6].

On the other hand, if the baseline for risk assessment is defined to be the quantification of particles, other approaches must be taken into consideration, mostly based on plasma techniques, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Liquid Chromatography-Mass Spectrometry (LC-MS), Laser-Induced Breakdown Spectroscopy (LIBS), among others [6].

Although there is a variety of existing quantitative approaches, nonetheless there is no ideal method to characterize nanomaterials and there are no standardized methods and sampling strategies, which represents a barrier to further studies in this area.

Currently, it is also possible to use direct-reading methods, which provide a fast and real-time response. These methods are capable of measuring a single compound or a wide range of them, and can be applied to area, process and personal monitoring [8]. They also provide on-site measurement, identifying short-term exposures, estimating long-term exposures and be used to produce, for example, an evacuation alarm. One of their great advantages is that they allow immediate results on-site, sparing unnecessary steps as collecting, storing and shipping samples [8]. The most common direct-reading devices that have been used for monitoring nanomaterials in workplaces' air are [8]:

- the Condensation Particle Counter (CPC);
- the Scanning Mobility Particle Sizer (SMPS);
- the Diffusion Charger (DC);
- the Electrical Low-Pressure Impactor (ELPI).

Nevertheless, although the use of these devices allows the identification, characterization and quantification of some nanomaterials, assessing the occupational risk based only in quantitative methods is still difficult since for many nanomaterials no OELs are defined and there is not enough knowledge about their potential effects. Additionally, most studies focus on manufactured nanoparticles [12], even if they only constitute a portion of the existing nanomaterials on the working atmosphere. The presence of nanomaterials that have not been produced with a certain purpose can make estimating and modelling exposure a real challenge [13]. For that reason, other methods are required to properly study the risks associated with the occupational exposure to nanomaterials, namely incidental ones.

2.2. Risk management regarding occupational exposure to nanomaterials – An overview on semi-quantitative and qualitative approaches

As mentioned previously, even though the importance to assess the risk associated with exposure to nanomaterials is clear, the quantification of it is full of uncertainties. For instance, the unknown contribution of a nanoparticle's physical structure to its overall toxicity, the lack of agreement on the relevant indices of exposure (for example, particle size and surface area are pointed as being more significant than mass), the little information on exposure scenarios and populations at risk [14] and the absence of toxicological data to establish OELs [15]. Facing these and other difficulties, the application of traditional risk assessment methods withdrawn, and qualitative risk assessment methods became more suitable and frequently used [15].

In the qualitative methods group, Control Banding (CB) is considered by several authors as an appropriate approach for assessing the exposure risk to nanomaterials [16] and is the one applied more frequently [9]. This methodology consists on a strategy for identification and recommendation of exposure control measures for potentially hazardous chemicals for which reliable toxicological and exposure information are limited [17], as it is the case of the exposure to nanomaterials. The designation Control Banding comes from the classification of these chemicals into "bands" (each one correspondent to a risk control strategy) that separate them into groups considering the hazard level of known chemicals similar to those being studied, subsequently assessing the risk and determining if there is a need for action [10].

In 2017, Dimou and Emond presented a literature review regarding control banding and proposed a semi-quantitative method for hazard assessment of nanomaterials to occupational health and safety. This review offered some examples of Control Banding methods applied by some authors to assess nanomaterials' exposure risk namely: Control Banding Nanotool (developed in the United States); Stoffenmanager Nano (The Netherlands); French Agency for Food, Environmental and Occupational Health & Safety CB Tool (France); NanoSafer (Denmark); The Guidance (The Netherlands); and Precautionary Matrix for Synthetic Nanomaterials (Switzerland).

These authors state that each of them has a particular scope and specific purpose. For example, NanoSafer and Stoffenmanager Nano focus on the assessment of occupational risk during the synthesis and downstream use of engineered nanomaterials in laboratories, CB Nanotool is very focused on nanotechnology researchers' protection and Precautionary Matrix for Synthetic Nanomaterials focuses on workers and consumers' protection.

After analysing these methods strengths and weaknesses, Dimou and Emond (2017) proposed a semi-quantitative methodology of CB based on physicochemical and biological characteristics of engineered nanomaterials and claim that this tool will protect workers that deal with manufactured nanomaterials and hazardous chemicals.

Apart from Control Banding, other risk analysis methods can be used to evaluate the risk regarding nanomaterials, as shown by Erbis et al. (2016), in their review regarding research trends and methods in nano environmental, health and safety risk analysis. Besides control banding, these authors highlight Monte Carlo Simulation Model, Decision tree analysis, Multicriteria decision analysis and Bayesian analysis.

Yet concerning risk management regarding exposure to nanomaterials, different concepts continue to emerge, such as safety by design approaches. For instance, Silva, Arezes and Swuste (2015) claim that a Systematic Design Analysis Approach (SYDAPP) allows taking a step forward in risk management, as it highlights risk control, rather than achieving only the results of a regular risk assessment. According to these authors, merging design analysis with the identification of the different exposure scenarios, makes it possible to percept how the diverse processes will affect the level of exposure. In addition, the authors state that, in the case of nanoparticles, it is relevant to be aware of the hazards from previous stages of the processes that involve their emission and exposure, and therefore achieve more efficient ways to control occupational risk.

First of all, the authors suggest applying the design analysis to a production process identifying: production functions (that splits the process into its core activities); production principles (recognizes the general process, motive power and operational control methods to reach the production function); and production forms (that specifies the detailed design to achieve the production principle). After that, emission and exposure scenarios shall be identified during regular operations, process disturbances, cleaning and maintenance activities, using Hazard and Operability Study (HAZOP) or an equivalent method. The third step consists in the identification of possible emission and exposure reduction barriers, followed by risk assessment for each operation (for example, using a control banding tool), assembling different production process alternatives based on the design analysis and finally repeating stages 2, 3, 5 and eventually 1, for alternative production processes.

As the design analysis approach focuses in risk control rather than in risk evaluation, it is suitable when dealing with nanotechnology occupational risks, being able to eliminate risks, prevent exposure and/or protect the workers [18].

Other more complex models for nanomaterials exposure have been developed, such as the conceptual model proposed by Schneider et al. (2011), which considers the main processes tangled in the transport of nanoparticles emitted from a source to a receptor [19].

As presented here, similar to quantitative approaches, qualitative and semi-quantitative methods for nanomaterials' exposure risk assessment are varied but not yet standardized and systematized.

2.3. Risk management regarding occupational exposure to nanomaterials during metal additive manufacturing – A literature review

To understand and study metal AM occupational risks, it is first of all essential to be conscious of the variety of feedstock materials and technologies that can be involved, and the particularities of all of them, keeping in mind that it is evolving and improving rapidly. Essentially, AM metal processing consists of using an energy source (laser or electron beam mainly) to melt metallic feedstock. Afterwards this melted material is transformed layer by layer making a solid part. DebRoy et al. (2018) state that the two main processes of AM processes for metallic components are directed energy deposition (DED) and powder bed fusion (PBF), as supported by Ngo et al. (2018), although this last publication refers other emerging techniques, such as binder jetting, cold spraying, friction stir welding, direct metal writing and diode-based processes. As for metallic feedstock in 3D metal printing, it is possible to use stainless steel, precious metals (for example gold, silver and platinum), several metal alloys, such as aluminium, titanium, nickel, cobalt and magnesium based alloys, among other metal materials. Ngo et al. (2018) also refer engineered nanomaterials as emerging feedstock materials for 3D printing, as they can drop sintering temperatures and improve electrical and mechanical properties. Nevertheless, it is believed that the exposure to nanomaterials during 3D printing processes is not exclusive to processes that add nanomaterials as a feedstock, being also relevant to study exposure to incidental nanomaterials during metal AM.

The present literature review took into consideration peer reviewed publications regarding nanomaterial emissions during metal AM, using two databases: ISI Web of Knowledge, from Thomson Reuters, and Scopus, from Elsevier. The keywords used in this research included “Metal Additive Manufacturing” or “Metal 3D Printing”, “Exposure to Nanomaterials” or “Exposure to Nano-objects” or “Exposure to Nanoparticles”, and “Risk Assessment” or “Risk Management”. Considering the fact that additive manufacturing was established in the late 1980s, the time period considered in the current article was between January 1990 and July 2018. The search was limited to peer-reviewed journals, thesis and other available online published documents, written in English. Another important criterion was that only studies performed in real occupational environments were considered, excluding simulations in possible controlled environments.

The searches resulted in a total of 18 registries to analyze. Studies that merely referred the risk of exposure but did not assess it were not considered, as well as those who did not assess the risk of occupational exposure to metal nanomaterials. Taken into account the inclusion criteria previously set and the scope of this literature review, two articles were considered eligible.

3. Results

During additive manufacturing procedures, nano-objects are released as shown in a considerable number of published studies. So far most of them have been focused on evaluating and characterizing the emitted pollutants emissions of 3D printers that use polymers, mainly acrylonitrile-butadiene-styrene (ABS) and polylactic acid (PLA) [2]. Nonetheless metal AM should also be emphasised in these studies, as metal nano-objects health effects are recognized in other metal manufacturing operations such as welding, namely long-term pulmonary effects (Andujar et al. 2014).

Having that conscious, Mellin et al. (2016) published a study regarding emission of nano-sized by-products in metal AM, specifically in selective laser melting (SLM) technology, and also in composite manufacturing and fabric production. Using Scanning Electron Microscopy (SEM), the authors found micron-sized particles in samples of recycled powder of a nickel base superalloy (Inconel 939) emitted by SLM process, that were within the respirable range, raising health and safety concerns, as the metal particles released contain sensitizing constituents (some elements, as Cobalt, are known carcinogens).

Even though this study focused only in SLM, the authors refer that evaporation is a problem in Electron Beam Melting (EBM) technology, that can hence the chance of occupational exposure to nano-sized particles, but no studies have been published in this field so far. As for control measures, this study suggests good ventilation equipment (with filters), personal breathing masks and the handling of the powder in a confined space. The authors suggest additional to add information in the safety data sheet for powder intended to be used in metal 3D printing.

One year later, Graff et al. (2017) published a related study, focused on the assessment of particle emission during additive manufacturing of metals, including nanoparticles. The AM technology studied was also SLM with metal powder, involving mostly chromium, nickel and cobalt. The assessment was carried out taking into account the number, mass, size and identities of particles, using Nanotracer (10 to 300 nanometres), Lighthouse Handheld Particle Counter (Handheld 3016 IAQ) (300 nanometres to 10 micrometres) and traditional filter-based particle mass estimation followed by inductively coupled plasma mass spectrometry. Apart from clearing the existence of risk to particle exposure in certain AM operations, namely exposure to nanosized particles in handling the metal powder, one of the interesting conclusions of this study was that the size of particles tended to be smaller in recycled metal powder compared to new. According to the authors, it would be imperative to improve powder handling systems and measurement techniques for nanosized particles, allowing the future development of work environment regulations. To this point, the recommendations were the use of personal protective equipment, improvement in powder handling systems, regular metal analyses of urine and regular analyses of the presence of metal in urine (biomonitoring for metals).

A compilation of both studies' relevant outputs regarding exposure to nanomaterials during metal AM can be found in table 1.

Table 1 – Outputs of the literature review on occupational risk management of exposure to nanomaterials during metal AM

	Graff et al. (2017)	Mellin et al. (2016)
Aim of the study	Study generated nano-sized by-products during production in metal 3D printing, composite manufacturing and fabric production	Use measuring techniques optimized for different particle sizes while analysing numbers, sizes, masses and identities of metal particle emissions
Metal material	Nickel-base Inconel 939 (both virgin and used powder)	Chromium, nickel and cobalt alloy (both virgin and used powder)
AM technique	Selective laser melting (SLM)	Selective laser melting (SLM)
Methods performed	<ul style="list-style-type: none"> • Scanning electron microscopy (SEM); • Energy Dispersive Spectrometer (EDS). 	<ul style="list-style-type: none"> • Nanotracer (10 to 300 nm); • Lighthouse (300 nm to 10 µm); • Traditional filter-based particle mass estimation and inductively coupled plasma mass spectrometry.
Main results	<ul style="list-style-type: none"> • Nanosized particles were generated during metal AM; • Presence of nanosized particles in samples with recycled powder. 	<ul style="list-style-type: none"> • Nanosized particles were generated during metal AM; • Operators were exposed mainly while handling powder; • Particle sizes tended to be smaller in recycled powder.
Control measures and other recommendations for risk management	<ul style="list-style-type: none"> • Powder handling in a confined space; • Personal protective equipment; • Good ventilation with HEPA filters; • Inclusion of information in the safety data sheet for powder intended to be used in metal 3D printing; • Educate workers. 	<ul style="list-style-type: none"> • Improve powder handling systems; • Measurement techniques for nanosized particles; • Work environment regulations; • Personal protective equipment; • Regular metal analyses of urine.

4. Conclusions

Metal Additive Manufacturing is an emerging technology that is becoming more common in occupational environments, having still many unknown and unstudied risks. Nowadays workers are already working side-by-side with machines that print 3D metal parts, using diverse technologies and various metal feedstock materials. Their routine may involve feeding metal powder to machines, brushing parts after printing, insuring maintenance operations, among other tasks that might have a serious impact on their safety and health conditions. One of the root causes for concern is the unintentionally generated nano-objects during metal AM processes, as their impact on health and the environment is not yet sufficiently clear.

Studies developed recently show emission of nanomaterials during metal 3D printing, even when no engineered nanomaterials are involved, rising concern and emphasizing the need for more investigation in this field. Studies reviewed in the current article focus on recognizing the presence of nanomaterials in these work environments, though no deep risk assessment is performed and no risk management methodology is even mentioned. It is important not only to be aware of the risk, but also to be able to assess and manage it, even though nowadays no risk management methodologies are proven to be totally credible and reliable.

Many doubts may occur when it comes to choosing the best approach for risk assessment of exposure to nanomaterials during metal AM, and particularly for risk management, but the importance of more investigation in this field is not called into question.

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